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Disclaimer

Laser activity at 1.18 μm, 1.07 μm, and 0.97 μm in the low phonon energy hosts KPb_2Br_5 and $RbPb_2Br_5$ doped with Nd^{3+}

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For the first time laser activity has been achieved in the low phonon energy, moisture-resistant bromide host crystals, neodymium-doped potassium lead bromide (Nd^{3+}:KPb_2Br_5) and rubidium lead bromide (Nd^{3+}:$RbPb_2Br_5$). Laser activity at 1.07 μm was observed for both crystalline materials. Laser operation at the new wavelengths 1.18 μm and 0.97 μm resulting from the $^4F_{5/2}+^2H_{9/2}\rightarrow^4I_J$ transitions (J=13/2 and 11/2) in Nd:RPB was achieved for the first time in a solid state laser material. Rare earth- doped MPb_2Br_5 (M=K, Rb) is a promising candidate for long wavelength infrared applications because of its low phonon frequencies and other favorable features. In principle, Nd^{3+}:MPb_2Br_5 has high potential for laser operation at new wavelengths as well as for the realization of short-wavelength lasing due to upconversion processes.

OCIS codes: (140.3380) Laser materials; (160.5690) Rare earth doped materials

Tunable Long Wavelength Infrared (LWIR) Lasers are beneficial compact sources e.g. for remote sensing in the vibrational fingerprint region (pollution monitoring), thermal scene illumination, and infrared spectroscopy in clinical and diagnostic analysis. For this purpose, we explore the potential of the rare earth doped KPb_2Br_5 (KPB) and $RbPb_2Br_5$ (RPB) crystals.[1] In this paper we report on room-temperature laser operation in KPB and RPB which has been achieved for the first time in a low phonon energy, moisture-resistant bromide host crystal to our knowledge. Laser operation in bromide crystals was previously demonstrated in Pr^{3+}:$LaBr_3$ and $PrBr_3$ which are known to be highly hygroscopic.[2] In this paper laser operation at 1.07 μm is reported by directly pumping into the $^4F_{3/2}$ level of a neodymium doped MPB (M=Rb, K) crystal. Laser activity at the new wavelength 1.18 μm resulting from the $^4F_{5/2}+^2H_{9/2}\rightarrow^4I_{13/2}$ transition in

Nd:RPB was achieved for the first time in a solid state material. In the same crystal laser activity at the wavelength 0.97 μm resulting from the $^4F_{5/2}+^2H_{9/2}\rightarrow^4I_{11/2}$ transition was also shown for the first time. In both cases the upper laser level was pumped directly at 0.81 μm.

The host crystals KPB and RPB evidence similar properties to the chloride crystal KPb_2Cl_5 (KPC) (also moisture resistant) but with the added advantage of even lower phonon energies. To achieve an acceptable quantum efficiency from a given energy level a rule of thumb demands that at least four to six (maximal energy) phonons span the energy gap to the next lowest level. Otherwise the luminescence is quenched, as is typical for fluorides and oxides emitting at wavelengths longer than 4 μm (with maximum phonon energies in excess of 500 cm^{-1}). With a maximum peak value of ~ 138 cm^{-1} (KPB) and ~ 141 cm^{-1} (RPB)[1] the phonon energy is ~ 1.5 times smaller than in KPC (203 cm^{-1})[3] because of the higher atomic masses of the vibrating bromine constituent. This minimizes the nonradiative decay due to multiphonon interactions, in principle permitting lasing in the long wavelength region (e.g. 10 μm with dopant ions like Tb^{3+}).[1] In KPC laser operation has been achieved with the rare earth ions Nd^{3+} (1.06 μm)[4], Dy^{3+} (2.43 μm)[5], and Er^{3+} (1.7 μm, 4.5 μm)[6].

Single crystals (up to 50 mm long) of KPB and RPB doped with Nd^{3+} were grown by the Bridgman technique from a stoichiometric mixture. Here, evacuated silica ampoules in a double-zone furnace, providing a temperature gradient of about 20°C/cm were used. KPb_2Br_5 and $RbPb_2Br_5$ have different crystal structures. The KPB crystal is biaxial and has a monoclinic crystal structure. The $RbPb_2Br_5$ crystal is uniaxial and has a tetragonal crystal structure. For further information we refer to one of our previous studies.[1]

The absorption spectra (Fig. 1) taken with a commercial Perkin-Elmer Lambda 9 spectrophotometer show peaks assigned to transitions of the Nd^{3+}-ion in KPB and RPB. In these spectra, absorptions due to long tails originating from the band edges at the shorter wavelengths have been substracted. In the Nd^{3+} doped RPB crystal we observed a strong dependence of absorption on polarization[1] which was taken into account during the laser experiments. The (blackbody corrected) emission spectrum of the Nd:MPB crystals (Fig. 1) was obtained by using a liquid nitrogen cooled InSb-detector, a ½ m, 1μm blaze grating (600 l/mm) monochromator, and a Ti:Sapphire laser to excite the $^4F_{7/2}$ level at a wavelength of 0.75 μm. The high emission rate of transitions originating from the $^4F_{5/2}+\,^2H_{9/2}$ level relative to the $^4F_{3/2}$ level demonstrates the greatly reduced nonradiative multiphonon decay rate of the bromide versus the chloride[3] (arising from the lower phonon energies). Strong upconversion fluorescence (e.g. due to emission from the $^4G_{7/2}$ level) was observed in the bromide crystals during the laser experiments. The long lifetime of the lower laser levels ^4I_J (J= 11/2, 13/2) leads to reabsorption processes and self-terminating laser activity. For these processes and for possible depopulation mechanisms we would like to refer to our forthcoming paper.[7] Emission cross sections have been independently determined for transitions from the $^4F_{3/2}$ level and $^4F_{5/2}$ level by using the Fuechtbauer-Ladenburg equation[8,1]. Here, radiative lifetimes of 208 μs ($^4F_{5/2}+^2H_{9/2}$) and 126 μs ($^4F_{3/2}$) for Nd:KPB and 214 μs ($^4F_{5/2}+^2H_{9/2}$) and 115 μs ($^4F_{3/2}$) for Nd:RPB were used, calculated assuming the high temperature statistical limit for the $^4F_{5/2}+^2H_{9/2}$ populations. Taking account of the finite temperature yields a slightly shorter $^4F_{5/2}+^2H_{9/2}$ radiative lifetime of ~ 150 μs, based on the crystal field assignments for the individual levels.

Laser activity for an uncoated Nd:KPB sample (l= 4.85 mm) and Nd:RPB sample (l= 7 mm) was achieved at 1.07 μm in both host materials in a nearly concentric cavity with two 100 mm concave laser mirrors (high reflector transmission for the pump wavelength of ~ 0.89 μm, output coupling of ~ 3% in KPB and 7.8% in RPB for the laser wavelength). An OPO system (~

10 ns pulse length, repetition rate 10 Hz) was used as a pump source. The pump spot size in the crystal was ~ 200 μm. While the Nd:KPC crystal showed laser activity for the $^4F_{3/2}$ – $^4I_{11/2}$ transition with the pump wavelengths 0.76 μm ($^4F_{7/2}$), 0.81 μm ($^4F_{5/2}$), and 0.89 μm ($^4F_{3/2}$) in the cavity described above, the Nd:KPB showed in our experiment lasing exclusively by pumping the $^4F_{3/2}$ level directly (Fig. 1). This could be explained by the difference in the measured lifetimes of the $^4F_{5/2}$ pumped levels of the chloride compared to the bromide crystal of 2 μs versus 124 μs (Nd:KPB) and 126μs (Nd:RPB)[1]. We determined the quantum efficiency $\eta_{^4F_{5/2}}$ to be 0.60 (Nd:KPB) and 0.59 (Nd:RPB) by taking the ratio of the measured lifetime and the calculated radiative lifetime (208 μs and 214 μs) for the $^4F_{5/2}$+$^2H_{9/2}$ level.[1] These are considerably higher values compared to the value of 0.013 reported for Nd:KPC,[3] again due to the lower phonon energies of the bromides. The laser threshold with the setup described above was reached at 4 mJ (Nd:RPB) and 1.6 mJ (Nd:KPB) incident pump energy for the 1.07 μm laser wavelength. For comparison we calculated a threshold of 0.9 mJ/pulse for Nd:KPB by assuming 40% losses per roundtrip and by neglecting possible influence of ESA. The pump energy absorbed is ~ 31 % in Nd:KPB and 56% for Nd:RPB by pumping with E parallel to the c-axis and lasing with E || c. 111 μJ (Nd:KPB) and 476 μJ (Nd:RPB) output was achieved with an incident pump energy of 9 mJ/pulse (maxium intensity of pump source) and the output coupling described above. The slope efficiency for Nd:KPB is determined from the data in Figure 2 to be 1.4 % which gives 4.5% for the output energy with respect to absorbed pump energy. The slope efficiency for Nd:RPB is determined from the data in Figure 2 to be 9.4 % which gives 16.8 % for the output energy with respect to absorbed pump energy.

In addition to the laser wavelength 1.07 μm the Nd:RPB crystal revealed laser activity at 0.97 μm and at 1.18 μm in the same cavity as described above by also pumping the upper laser level at 0.81 μm directly (Fig. 1). Here, we used an output coupling of 0.2% for 0.97 μm and 0.5% for 1.18 μm. The laser threshold was reached at ~ 6.5 mJ incident pump energy for 0.97 μm, and at 6.1 mJ for 1.18 μm. 68 μJ output was achieved with an incident pump energy of 9 mJ/pulse at 1.18 μm, while approximately one third the output was achieved at 0.97 μm (not shown in figure). The pump energy absorbed is 72% for Nd:RPB by pumping with E parallel to the c-axis. The slope efficiency for Nd:RPB is determined from the data in Figure 2 to be 2.2 % which gives 3.1 % for the output energy with respect to absorbed pump energy. Possible presence of ESA at ~ 1.2 μm can also explain the laser activity at the peak wavelength 1.18 μm. Tunability may well be possible at these new wavelengths resulting from the $^4F_{5/2}$ level in the bromide crystals (Fig. 1). We will continue our laser experiments by using a pump source with longer pulse length in order to increase the pump energy.

We reported on Nd^{3+} doped KPB and RPB as new room temperature solid state laser materials. Laser activity has been achieved in low phonon energy, moisture-resistant bromide host crystals. Laser activity at 1.07 μm was achieved by directly pumping into the $^4F_{3/2}$ level. Laser operation at the wavelengths 1.18 μm and 0.97 μm resulting from the $^4F_{5/2}+^2H_{9/2}\rightarrow^4I_J$ transition (J=13/2 and 11/2) was achieved in Nd:RPB for the first time in a solid state laser material. The nonradiative decay competes less effectively compared to the radiative rate in these rare earth doped bromide host crystals. Higher quantum yields have been achieved in the bromide host crystals compared to the KPC crystals for transitions from the $^4F_{5/2}$ level into the ^4I_J levels in Nd:MPB (M= K, Rb), which makes lasing at new wavelengths feasible. Strong upconversion fluorescence was observed in the bromide crystals which also makes short-wavelength lasing in these crystals possible. However, the accumulation of population in the lower laser level favors pulsed operation over the cw mode in these rare earth doped bromide materials, although depopulation of the lower laser levels by cross relaxation may permit cw operation at higher Nd concentration.

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REFERENCES

[1] K. Rademaker, W. F. Krupke, R. H. Page, S.A. Payne, K. Petermann, G. Huber, A.P. Yelisseyev, L.I. Isaenko, U.N. Roy, A. Burger, K.C. Mandal, K. Nitsch, "Optical properties of Nd^{3+} and Tb^{3+} doped KPb_2Br_5 and $RbPb_2Br_5$ with low nonradiative decay", J. Opt. Soc. Am. B **x**, in press (2004)

[2] A.A. Kaminskii, Crystalline Lasers: Physical Processes and Operating Schemes (CRC Press, New York, 1996)

[3] M.C. Nostrand, R.H. Page, and S.A. Payne, L.I. Isaenko, A.P. Yelisseyev, "Optical properties of Dy^{3+}- and Nd^{3+}-doped KPb_2Cl_5", J. Opt. Soc. Am. B **18**, no. 3, 264-276 (2001)

[4] M.C. Nostrand, R.H. Page, S.A. Payne, W.F. Krupke, P.G. Schunemann, L.I. Isaenko, "Laser demonstrations of rare-earth ions in low-phonon chloride and sulfide crystals", Advanced Solid State Lasers, H. Injeyan, U. Keller, C. Marshall (eds.), OSA TOPS 34, Opt. Soc. Am., 459-463 (2000)

[5] M.C. Nostrand, R.H. Page, S.A. Payne, W.F. Krupke, P.G. Schunemann, L.I. Isaenko, "Room temperature $CaGa_2S_4:Dy^{3+}$ laser action at 2.43 and 4.31 μm and $KPb_2Cl_5:Dy^{3+}$

laser action at 2.43 μm”, Advanced Solid State Lasers, M.M. Fejer, H. Injeyan, U. Keller (eds.), OSA TOPS 26, Opt. Soc. Am., 441-449 (1999)

[6] S.R. Bowman, S.K. Searles, N.W. Jenkins, S.B. Qadri, E.F. Skelton, J. Ganem, “New mid-IR laser based on an erbium activated low phonon energy crystal”, Technical Digest of conference on Lasers and Electro-Optics CLEO 2001, Baltimore, Maryland, USA, 557-558 (2001)

[7] K. Rademaker, G. Huber, S.A. Payne, E. Osiac, L.I. Isaenko, “Optical pump-probe processes in Nd^{3+} doped KPb_2Br_5, $RbPb_2Br_5$, and KPb_2Cl_5”, will be submitted to xxx (2004)

[8] B.F. Aull, H.P. Jenssen, “Vibronic interactions in Nd:YAG resulting in nonreciprocity of absorption and stimulated emission cross sections”, IEEE J. Quant. Electr. **QE-18**, no. 5, 925-930 (1982)

REFERENCES (no titles)

[1] K. Rademaker, W. F. Krupke, R. H. Page, S.A. Payne, K. Petermann, G. Huber, A.P. Yelisseyev, L.I. Isaenko, U.N. Roy, A. Burger, K.C. Mandal, K. Nitsch, J. Opt. Soc. Am. B **x**, in press (2004)

[2] A.A. Kaminskii, Crystalline Lasers: Physical Processes and Operating Schemes (CRC Press, New York, 1996)

[3] M.C. Nostrand, R.H. Page, and S.A. Payne, L.I. Isaenko, A.P. Yelisseyev, J. Opt. Soc. Am. B **18**, no. 3, 264-276 (2001)

[4] M.C. Nostrand, R.H. Page, S.A. Payne, W.F. Krupke, P.G. Schunemann, L.I. Isaenko, Advanced Solid State Lasers, H. Injeyan, U. Keller, C. Marshall (eds.), OSA TOPS 34, Opt. Soc. Am., 459-463 (2000)

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[6] S.R. Bowman, S.K. Searles, N.W. Jenkins, S.B. Qadri, E.F. Skelton, J. Ganem, Technical Digest of conference on Lasers and Electro-Optics CLEO 2001, Baltimore, Maryland, USA, 557-558 (2001)

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[8] B.F. Aull, H.P. Jenssen, IEEE J. Quant. Electr. **QE-18**, no. 5, 925-930 (1982)

Inscription of the Figures:

1. Absorption and emission spectra of Nd^{3+} doped MPb_2Br_5 (M=K, Rb) shows peaks assigned to transitions of the Nd^{3+} ion. The blackbody corrected room temperature emission spectra are obtained by excitation of the $^4F_{7/2}$ level. Compared to the KPb_2Cl_5:Nd^{3+},[2] the more intense fluorescence from the $^4F_{5/2}$ level (= $^4F_{5/2}$+ $^2H_{9/2}$ level) due to the low multiphonon decay rate was encouraging for achieving possible laser activity at new wavelengths.

2. Input-output characteristic for an OPO pumped Nd:KPB crystal lasing at 1.07 μm and Nd:RPB crystal lasing at 1.07 μm and 1.18 μm. The slope efficiency is given for output pulse energy with respect to absorbed pump energy. In order to achieve lasing at 1.07 μm the $^4F_{3/2}$ level was

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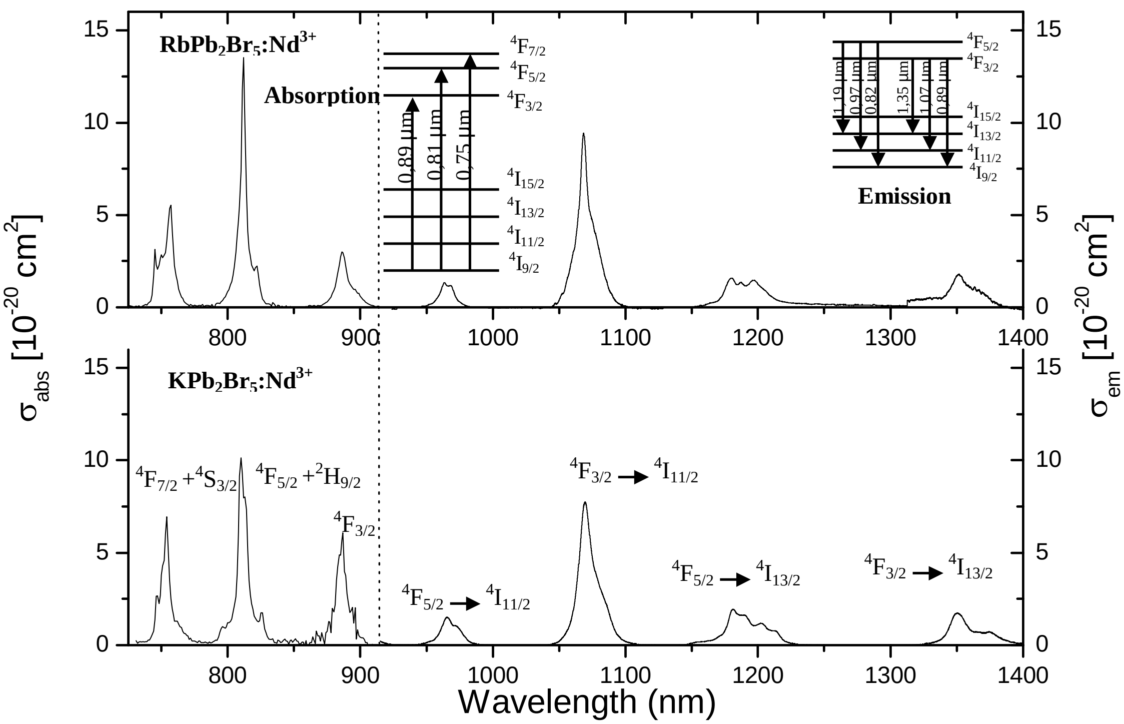

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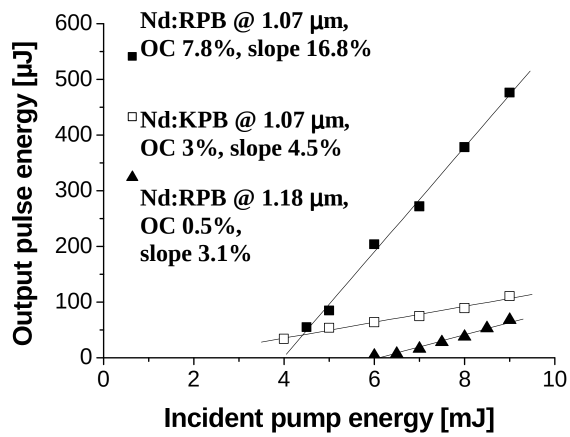

Fig. 2. Input-output characteristic for an OPO pumped Nd:KPB crystal lasing at 1.07 µm and Nd:RPB crystal lasing at 1.07 µm and 1.18 µm. The slope efficiency is given for output pulse energy with respect to absorbed pump energy. In order to achieve lasing at 1.07 µm the $^4F_{3/2}$ level was directly pumped, while for the laser wavelength 1.18 µm and 0.97 µm the $^4F_{5/2}$ level was pumped.